EFFECT OF PHYSICOCHEMICAL PROCESSES IN FIREPROOF MATERIALS ON THEIR THERMAL CONDUCTIVITY

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The relationship between the effective thermal conductivity of fireproof materials with heterogeneous phase transitions and chemical transformations and diffusion processes in the pores and microfissures is demonstrated.

In [1-3] the relationship of the effective thermal conductivity of fireproof materials in vacuum with the pressure of gas located in a vacuum chamber (passive gas) and emanating from a solid phase (active gas) has been investigated. However, the natures of interaction of passive and active gases with the solid phase are substantially different, since the formation and absorption of the latter is related to expenditure of a definite amount of heat. Therefore, if there are sources and regions of absorption of "active molecules" in a system, then directional mass transfer, accompanied by energy transfer as in the case of a chemically reactive gas mixture [14], appears. This mass transfer can occur in pores and microfissures under conditions of a temperature gradient.*

We consider a closed plane slit filled by an active gas. Under isothermal conditions the composition of the gas mixture corresponds to equilibrium and is determined by the joint action of the phase conversions, heterogeneous chemical reactions, and other processes; there are no effective fluxes of molecules. In the case when the walls of the slit have different temperatures, the partial pressures of gas-forming substances at different points of the microvolume will no longer be identical, which leads to a directional transport of molecules.

The existence of a special mechanism of heat transfer in nonisothermal cavities, which is inherent to only an active gas, must be taken into consideration in investigating the effect of microfissures and pores on the thermophysical characteristics of heterogeneous materials. The effective thermal conductivity of a layer of thickness $\delta(\lambda_\sigma)$ will depend on the thermal conductivity of the mixture of the passive and the active gases ($\lambda_\delta{}^{n,a}$), the radiative component of the thermal conductivity (λ_δ^R), and will also include the component related to the mass transfer in the gaseous phase (λ_E^a).

Assuming the independence of the above components of the thermal conductivity, we can write

$$\lambda_\delta = \lambda_\delta^{n,a} + \lambda_\delta^R + \lambda_E^a, \tag{1}$$

where the terms $\lambda_\delta^{n,a}$ and λ_δ^R are computed from the well-known formulas recommended in [5-8]. The thermal conductivity of a single-component gas can be written in the following form, taking into consideration the dimensions of pores [5]:

$$\lambda_\delta^a = \lambda_0^a \left(1 + \frac{\Pi T}{p\delta}\right)^{-1}, \tag{2}$$

where

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*The basic scheme of computations was proposed by E. Ya. Litovskii.

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$$\Pi = \frac{2\sqrt{2}\,\frac{c_p}{c_v}\,(2-\alpha)\,k}{\pi d^2 \alpha \,\mathrm{Pr}\left(\frac{c_p}{c_v}+1\right)}\,.$$

Here λ_0^a is the thermal conductivity of the gas at normal pressure; p is the gas pressure in the pore; T is the temperature; Pr is the Prandtl number; c_p and c_v are the specific heats of the gas at constant pressure and constant volume; d is the diameter of the gaseous molecules; α is the accommodation coefficient; and k is Boltzmann's constant.

The radiative component of thermal conductivity [6] is

$$\lambda_\delta = 4f\sigma\delta T^3, \tag{3}$$

where $0 < f < 1$; f is a coefficient depending on the shape, size, and degree of blackness of the pore walls; σ is the Stefan–Boltzmann constant.

In computing the term λ_E^a in formula (1), one should remember that under low-pressure conditions the dimensions of the gas-filled cavities in porous bodies — ceramics, fireproof materials, metalloceramic moldings — are generally smaller than the mean free path of the gas molecules. In this case one can restrict the investigation only to heterogeneous processes leading to the formation of one gas product and neglect the reactions occurring in the gaseous phase. Let the walls of the slit have temperatures T_1 and T_2 (for definiteness we take $T_1 < T_2$). For $\Delta T \ll T_1$ the partial pressures of the reaction products will be only slightly different from the equilibrium pressures at temperatures T_1 and T_2, respectively, and for computing the number of molecules transferred from the hot surface to the cold surface and vice versa it is permissible to use the formulas derived from the molecular-kinetic theory of gases [9]. Then it can be shown that the effective flux of molecules of i-th type is related to their heat of formation ΔH by the relation

$$\Delta n_i = \frac{\alpha_i P x_i N}{T\sqrt{2\pi M_i R T}}\left(\frac{\Delta H_i}{RT} - \frac{1}{2}\right)\Delta T, \tag{4}$$

where P is the total equilibrium pressure, x_i is the molar fraction of the gas with molecular weight M_i, N is Avogadro's number, R is the gas constant, $\Delta T = T_2 - T_1$, $T = (T_1T_2)^{1/2}$, and α_i is the reflection coefficient for molecules of the i-th type during collision with the given surface.

From (4) we obtain a formula for the thermal conductivity λ_E^a for simultaneous occurrence of m independent processes at the surface of the slit:

$$\lambda_E^a = \frac{P\delta}{RT^2\sqrt{2\pi RT}} \sum_{i=1}^{m} \frac{\alpha_i \Delta H_i^2 x_i}{\sqrt{M_i}}\,. \tag{5}$$

It must be stressed that in a number of cases (dense and compacted fireproof materials) formulas (4) and (5) are valid also for continuous evacuation of the gaseous products, since in thin pores and microfissures the pressure differs very little from the equilibrium pressure because of their large hydraulic resistance and high rate of gas formation [3]. At the same time, in samples with large pores during intensive evacuation the departure of the gaseous products of reaction from the equilibrium pressure can be significant, which must be taken into consideration in the interpretation of the experimental results. Furthermore, under conditions of intense heat fluxes, which are typical, for example, for ablation, the mass transport becomes so intense that the effective thermal conductivity will be a function of the edge conditions. For a majority of fireproof materials under normal conditions of operation the kinetic effects are small and the thermal conductivity is practically a property of the material.

In fireproof materials diverse physicochemical processes of formation of the active gas may occur. In order to predict the temperature dependence of the thermal conductivity of different fireproof materials it is advisable to separate out the following reactions and phase transitions:

1) reaction of decomposition of solid compounds, mixtures, and the products of the interaction of the basic materials with the atmosphere, moisture, and furnace gases; for example,

$$MgCO_{3s} \rightleftarrows MgO_s + CO_{2g}{}^{*)}, \qquad \text{I}$$

$$CaCO_{3s} \rightleftarrows CaO_s + CO_{2g}, \qquad \text{II}$$

$$2Fe_2O_{3s} \rightleftarrows 4FeO_s + O_{2g}, \qquad \text{III}$$

$$n\,SiO_2 \cdot K_2O_s \rightleftarrows n\,SiO_{2s} + K_2O_g; \qquad \text{IV}$$

2) the reaction of interaction with gaseous substances — especially with water vapors — with formation of volatile compounds:

$$SiO_{2s} + 2H_2O_g \rightleftarrows Si(OH)_{4g}, \qquad \text{V}$$

$$BeO_s + H_2O_g \rightleftarrows Be(OH)_{2g}, \qquad \text{VI}$$

$$n\,SiO_2 \cdot K_2O_s + H_2O_g \rightleftarrows n\,SiO_{2s} + 2KOH_g \qquad \text{VII}$$

(it should be mentioned that on the basis of this type of reaction a transition of high-melting oxides at temperatures appreciably lower than their melting or sublimation temperature into the gaseous phase is possible);

3) phase transition: evaporation (sublimation) and condensation with participation of both the basic components of the fireproof material and the mixture:

$$MgO_s \rightleftarrows MgO_g, \qquad \text{VIII}$$

$$SiO_{2s} \rightleftarrows SiO_{2g}, \qquad \text{IX}$$

$$SiO_s \rightleftarrows SiO_g. \qquad \text{X}$$

On the basis of these examples we can infer the presence of sources of active gas practically in all fireproof materials; this fact should be taken into consideration in the analysis of the effective thermal conductivity. The thermodynamic analysis of many reactions shows a significant shift of the equilibrium toward the formation of gaseous products even at moderate temperatures up to 1000°C.

As an example, the temperature dependence of the thermal conductivity of the gaseous product in the absence of a chemical interaction of the gas molecules with the wall and in the presence of such an interaction is shown in Fig. 1 for two of the reactions discussed above. The parameter λ_E^{α} was calculated from Eq. (5); the equilibrium pressures p_i were determined from thermodynamic characteristics of the reaction [10]; the values of λ_δ^{α} and λ_δ^{R} were obtained from formulas (2) and (3); α was taken equal to 0.1 and 1 (according to experimental data presented in [9] for pure oxides $0.2 < \alpha < 0.8$).

As seen from Fig. 1, even at relatively low temperatures and, correspondingly, at low partial pressures of the active gas (2-3 orders of magnitude smaller than the atmospheric) its contribution to the total thermal conductivity can be very significant, so that under low-pressure conditions in the vacuum chamber the thermal resistance of the microfissures and the pores in a heterogeneous material will decrease with the increase of the temperature and may take values even lower than the thermal resistance of the microvolume filled by air at atmospheric pressure.

The above analysis of the role of the physicochemical transformations in heat and mass transfer inside pores permits one to draw a number of conclusions about the effect of these processes on the effective thermal conductivity of the material and also to note certain accompanying effects.

1. Due to the shunting of the thermal resistance of microfissures with the increase of the temperature of evacuated ceramics the effective thermal conductivity of the material (λ_m) must increase, in a number of cases reaching and even exceeding the value of λ_m measured at normal pressure of the external medium. Such results are typical for dense and compacted fireproof materials [1, 2]. The nonmonotonic dependence $\lambda_m(T)$ (Figs. 2 and 3) is also explained from these points of view. The data on the thermal conductivity and thermal diffusivity were obtained using the equipment and methods described in [11].†

2. Since according to formula (5) the thermal resistance of the microfissures depends on their thickness (for identical overall porosity), λ_m will be a function of the size dis-

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*Here and below the subscript "s" denotes the solid phase and "g" the gaseous phase.

†The measurements were made with the participation of I. D. Zborovskii, Ya. A. Landy, and N. A. Puchkelevich.

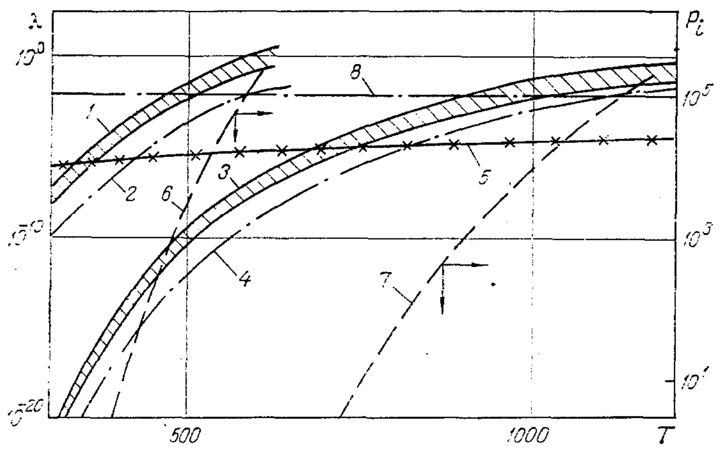

Fig. 1. The dependences of the components of the effective thermal conductivity λ [W/(m²•deg) of microfissures [formula (1)] and equilibrium pressure P (N/m²) inside the microfissure on temperature T (°K): 1, 3) $\lambda^{a}_{E}(T)$; 2, 4) $\lambda^{a}_{\delta}(T)$; 5) $\lambda^{R}_{\delta}(T)$ for f = 1; 6, 7) p_i; 8) thermal conductivity of slit filled with air at normal pressure. Thickness of the slit $\delta = 10^{-7}$ m. Curves 1, 2, and 6 correspond to reaction (I) occurring at the walls of the slit and curves 3, 4, and 7 to reaction (II). The hatched region corresponds to the change of reflection coefficient α_i from 0.1 to 1.

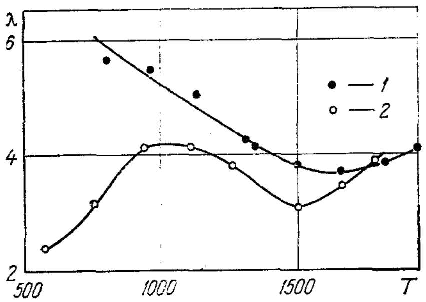

Fig. 2

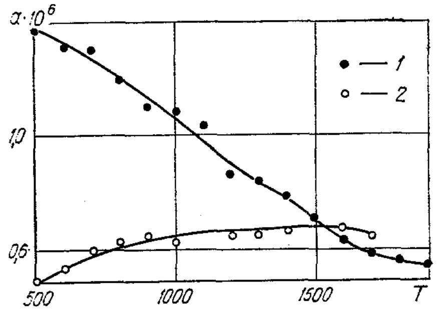

Fig. 3

Fig. 2. Temperature dependence of the thermal conductivity of the magnesite of normal density. Passive gas — argon: 1) pressure in chamber 10^5 N/m²; 2) $1.3 \cdot 10^{-2}$ N/m²; apparent density 2.57 g/cm³; open porosity 26.7%. Composition: MgO, 92.7%; CaO, 2.4%; Al_2O_3, 0.7%; Fe_2O_3, 1.4%; SiO_2, 2.6%.

Fig. 3. Temperature dependence of thermal diffusivity of magnesite chromite MKhVP. Passive gas — nitrogen: 1) pressure in the chamber 10^5 N/m²; 2) $1,3 \cdot 10^2$ N/m². Apparent density 3.21 g/cm³; open porosity 12.9%. Composition: MgO, 79.7%; Cr_2O_3, 11.0%; CaO, 1.4%; Al_2O_3, 2.1%; Fe_2O_3, 4.6%; SiO_2, 0.9%.

tribution of the pores. Furthermore, it may be expected that for thin layers of highly porous heat-insulating materials in vacuum λ_m should depend on the thickness of the sample and the physicochemical properties of the bounding surfaces. Similar dimensional effects are characteristic for radiative-conductive heat transfer [6, 8, 12].

3. The separation into "active" and "passive" gases done in [1-3] and in the present article is to a large extent arbitrary, since in many cases an interaction of passive molecules with the surface of the materials is possible. The latter can have catalytic properties or may be capable of dissociation, excitation, and other processes related to absorption or release of energy by the gas molecules. Furthermore, at high temperatures reactions between the "passive" and "active" molecules are possible, which will also lead to the de-

crease of the thermal resistance of the microfissures. The contribution of these reactions can be significant when a large probability of collision of the gas molecules exists; i.e., their mean free path is much smaller than the dimensions of the cavities in the solid. However, in this situation it is necessary to investigate the heat transfer in a chemically reacting gas mixture [4] and λ_δ (and, correspondingly, λ_m) may change with temperature nonmonotonically.

4. The energy transfer with the participation of the active gas must lead to definite changes in the structure of the sample. In particular, when the main component of the material is involved in the reaction (reactions V and VI) or in the presence of sublimation (VIII and IX), a displacement of the material from one surface of the microfissure or the pore to another, which is equivalent to the migration of the microvolume in the opposite direction, will be observed. In contrast to the case investigated earlier [13], the motion may occur both in the direction of the temperature gradient as well as against the gradient (depending on the sign of ΔH). The computation using Eq. (4) shows that for heat fluxes of 10^3-10^4 $W \cdot m^{-2}$ the rate of migration may reach 10^{-9}-10^{-7} m/sec. Similar results have been detected experimentally in metals [14, 15] and ceramics [13, 16, 17] located in a temperature gradient. Moreover, the formation and decomposition of volatile hydroxyls (reactions V and VI) under certain conditions cause transport of microscopic amounts of the substance [18].

5. It is very important to note that the change in the concentration of the mixtures due to mass transfer in the gas must be accompanied by the development of surface and volume diffusion fluxes to the wall and closing of the pores and microfissures. Since the diffusion mechanism in a solid is sufficiently complex and the ensuing concentration gradients and the diffusion paths can only be inferred qualitatively, it is very difficult to compute the diffusion fluxes. However, given reasonable orders of magnitude of the concentration gradients at the walls of the microfissures and assuming that the entire heat flux Q through the microfissures (known from experiment) is transferred due to the physicochemical processes occurring there, the diffusion coefficients ensuring the equality of the fluxes of the substance through the gaseous layer in the solid can be estimated from Fick's law. For the estimates we specify the following initial data: specific thermal flux through the microfissure $Q = 10^3$-10^5 W/m^2; grad $T = 10^4$ deg/m; the processes of heat and mass transfer caused by the substance with $M = 5 \cdot 10^{-2}$ kg/mole; $\rho = 3 \cdot 10^3$ kg/m^3; $\Delta\rho/\rho \cdot 100\% = 1\%$; cross section of the slit 10^{-8} m^2, its thickness 10^{-7} m; diffusion occurs in a surface layer of thickness 10 Å. Under such assumptions the maximum value of the surface diffusion coefficient which will be sufficient for complete isolation of the mass from the hot wall to the cold wall is 10^{-9}-10^{-5} cm^2/sec, which lies in the range of experimentally determined coefficients of self- and heterodiffusion for large-angle boundaries in polycrystalline materials (for example, see review [15]).

Thus, during the heat transfer in porous fireproof materials mechanisms similar to the processes in thermal tubes [6] occur: the heat and mass transport in the presence of heterogeneous phase reversals and inverse diffusion mass transfer. The thermal-tube mechanism explains the temporal stability and the reproducibility of the temperature dependence of the thermal conductivity in vacuum. Due to the gradual degassing of ceramics with repeated experiments and prolonged holding of the samples in vacuum only a small hysteresis of the thermal conductivity is observed [1, 2].

6. The presence of mixtures at integrain boundaries, the walls of the pores, and the microfissures must leave a definite impression on the nature of variation of the structure of the fireproof material in a temperature gradient field and, in particular, must lead to a decrease of the mobility of the boundaries. Thus, if the grain boundary comes in contact with the inclusion of an easily decompressible mixture as it is displaced, the increase of the pressure in the pore leads to a decrease of the temperature drop ΔT (for the same heat flux) and, hence, the motion of the boundary is retarded. We note that the decrease of temperature drop in the microcavity due to any process, for example, intense energy transfer resulting from heterogeneous or homogeneous (gaseous phase) reactions with the participation of the mixtures and radiative transport in holes, must reduce the rate of mass transfer of the basic material. The retardation of the rate of migration of the boundaries has been frequently observed in experiments [15, 19].

These effects associated with the change of the structure of fireproof materials in a temperature gradient field along with the direct results on thermal conductivity and temperature diffusivity of heatproof materials in a wide range of temperatures and pressures of the gaseous medium indicate the correctness of the proposed mechanism.

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A METHOD OF MEASURING HEAT CONDUCTION IN A QUASISTEADY MODE WITH ASYMMETRIC BOUNDARY CONDITIONS AND WITH ALLOWANCE FOR NONLINEARITY

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The allowance for the dependence of the coefficient of thermal conductivity on the temperature and the accuracy of maintenance of the boundary condition in the absolute method of measurement of heat conduction in a quasisteady mode with asymmetric coundary conditions is analyzed by the methods of perturbation theory (iteration method).

The use of the relationships of a quasisteady mode with asymmetric boundary conditions [1] to determine the coefficient of thermal conductivity was evidently done most successively by Kaganer in measuring the properties of vacuum-shield insulation [2]. In his method a linear (or close to it) temperature rise was created at one boundary of the test specimen,

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